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Leaching and releasing characteristics and regularities of Sb and As from antimony mining waste rocks

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This study collected waste rock samples during antimony mining and then probed into the releasing characteristics and regularities of heavy metals Sb and As under different factors (solid-to-liquid ratio, particle size, temperature, agitation intensity, pH value of leaching solution and leaching intensity) through indoor static soaking and dynamic leaching experiment. The results showed that: the smaller solid-to-liquid ratio, smaller particle size, or higher soaking liquid temperature could achieve the faster dissolution and precipitation rate of heavy metals; agitation could accelerate the dissolution and precipitation of heavy metals; the lower pH value could help to obtain more heavy metals deposited; the higher leaching intensity could make the rate of heavy metal reach the precipitation peak faster. Meanwhile, an equation fitting was conducted to the changing situation of Sb and As precipitation amount from antimony waste rocks with different influence factors under static and dynamic leaching, and the fitting results were good. This study was to reveal the releasing characteristics of heavy metal Sb and As in antimony mining waste rocks, so as to promote the harmonious development of metal mines.

Introduction

minerals [2, 3]. A large number of untreated waste rocks are usually transported directly to the stacking area and exposed to the surface for a long time. Under the action of rain, the precipitation of heavy metals from waste rocks will threaten the mining area environment health and surrounding residents [4, 5], especially that the leaching of Sb and As will cause extreme damage to the surrounding environment [6-8].

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antimony waste rocks. Wang et al. [9] studied the chemical composition of solid waste and smelting waste in an antimony mining area, and the results showed that in solid waste, the amount of solid waste released from antimony ores and smelting scrap metal was not proportional to the heavy metals. The research conducted by Zhang et al. [10] on antimony sulfide mine tailings showed that: the presence of sulfur-oxidizing bacteria could promote the leaching of heavy metals from antimony ores. The studies of B.A. Buchholz et al. [11] on municipal solid waste showed that the pH value of acid was an important factor controlling the concentrations of metals (As, Cd, Cu, Hg, Pb, S, and Zn) in leaching solution. K Moussaceb et al. [12] studied the leaching conditions of various chemical elements obtained in cement materials, and the results showed that solid ratio had an important influence on the leaching kinetics of target elements. Biver et al. [13] conducted an oxidation-solution release kinetic study on stibnite (Sb_2S_3) under different dissolved oxygen saturation degrees (0~80%) and different temperatures (25~48°C), which showed that the higher concentration of dissolved oxygen and higher temperature could make the dissolution release rate of stibnite faster, and they also presented the empirical equation for dissolution and release of stibnite.

For this purpose, by taking antimony mining waste rocks as the research object, this paper probed into the optimal release conditions of Sb and As in mining waste rocks through static soaking and dynamic leaching test, and analyzed the characteristics of dynamic leaching release so as to help promote the development of metal mines.

Materials and Methods

Test Materials

The mining waste rocks needed in the test were selected from the waste rock yard of north antimony mine. Samples were store for later use after being collected in the field, naturally dried in the lab, pulverized by the pulverizer (XMQ Φ 240 x 90, Jiangxi Ganye), and then sieved by 20-mesh, 40-mesh and 100-mesh nylon sieves.

Static Leaching Test

The device for static leaching test consisted of a thermostatic shaking bath and a wide-mouthed bottle, and the shaking bath was used to ensure that the temperature was consistent with external disturbance factors. A ground stopper glass bottle with a capacity of 1000 ml was used in the test. During the test period (15 days), the supernatant solution in the reagent bottle was extracted at an interval of 24 hours, and filtered by an injection-type filter with PE film (hole diameter = 0.2 μm).

Dynamic Leaching Test

A series of graduated organic glass columns were used in the dynamic leaching column to ensure the simultaneous leaching test (as shown in Fig. 1). The leaching column was 5 cm in radius and 50 cm in length, with the bottom sealed by an organic glass plate and retained a $\Phi 10$ mm round hole, and the leaching column was enclosed with $\Phi 2-3$ μm non-woven fabric at the bottom to prevent the loss of samples, and two layers of qualitative filter paper, 5 cm clean inert quartz sand (particle diameter of 0.6-1.0 mm) (ensure uniform water distribution), and sample (500 g) were placed in the leaching column successively from top to bottom.

For the leaching test at different pH (4.0, 5.0, 6.0), the leaching amount was 600 mL per day, lasting for 12 days, and a parallel control group was set for each kind of waste rock. The samples in the leaching column should be pretreated with reverse water saturation before testing so as to ensure consistent test conditions.

For the leaching tests at different intensities, the speed of the peristaltic pump was adjusted to 60 mL/h, 120 mL/h, and 180 mL/h, respectively. After the completion of leaching, the samples were collected for the measurement of Sb and As in the leaching solution.

Analysis Methods

A ZEE nit700 flame-graphite furnace atomic absorption spectrometer was used to determine the concentration of heavy metals, Sb and As in underground leaching solution, and a PB-10 acidity meter was used to determine the pH value of leaching solution, and the parabolic diffusion equation was used for fitting the release rule of Sb and As under dynamic leaching time.

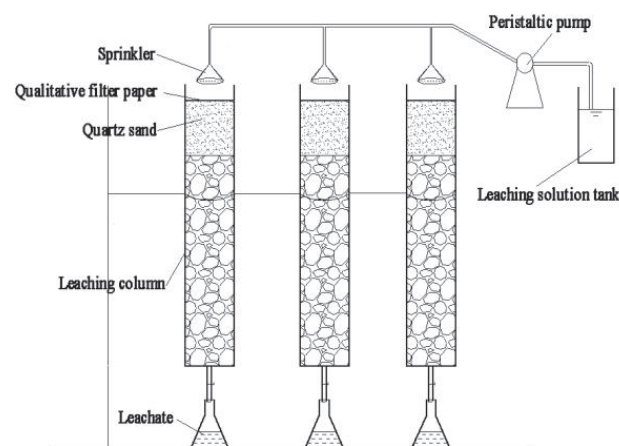


Fig. 1. Experimental device of dynamic leaching.

Results and Discussion

Effect of S/L on Sb and As Release

The changing curve of Sb and As leaching concentration over time under soaking conditions at different solid-liquid ratios is shown in Fig. 2. It could be seen from the figure that when the solid-liquid ratio was small ($S/L = 1:20$), the Sb and As concentration in soaking liquid was low, but the concentration gradient was larger; as the solid-liquid ratio increased, the Sb and As concentration in soaking liquid increased accordingly, but the concentration gradient decreased. Therefore, with the decrease in solid-liquid ratio, dilution played a dominant role in the effect of different solid-liquid ratios on the concentration of heavy metal in leaching solutions of antimony mining waste, and the leaching concentrations of Sb and As decreased successively. The calculation results showed that the total leaching amount of Sb and As in unit mass was increasing, which might be because the small solid-liquid ratio was more conducive to the precipitation and dissolution equilibrium of indissoluble minerals moving toward dissolution [14, 15].

It could be seen from the effect of soaking time on the release of heavy metal pollutants, Sb and As from antimony waste rocks that, with the passage of time,

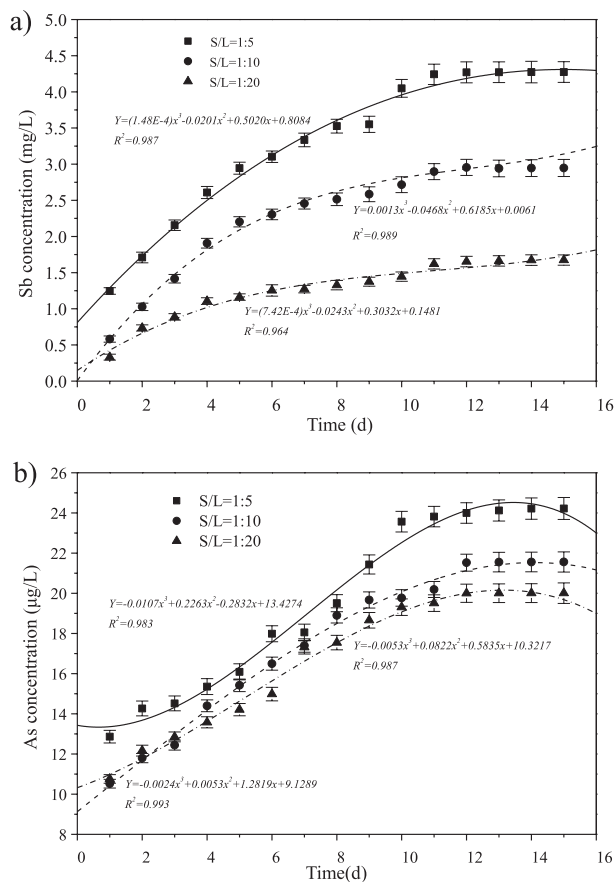


Fig. 2. Effect of S/L on a) Sb and b) As release in static experiment.

the concentration of Sb and As in soaking solution were on the rise, and it became stable in the 10th-15th days of soaking compared with the previous stage, and the reason might be that the precipitation of heavy metals from antimony mining waste in the previous 10 days was mainly surface dissolution, and then the dissolving precipitation process transferred to the inside of mining waste rocks; the precipitation of heavy metals mainly depended on the diffusion rate of antimony mining waste in the internal stoma, and the process was very slow, so the increase in heavy metal concentration became gradually stabilized. The regression fitting equation is shown in Fig. 2. It could be seen from the figure that the R^2 values of Sb and As regression release equations in waste rocks under different solid-liquid ratios were greater than 0.96, showing the better fitting effect.

Effect of Particle Size on Sb and As Release

For the waste rocks of different particle sizes, the variation curve of leaching concentration of each heavy metal over time was drawn according to the release of Sb and As under soaking conditions, as shown in Fig. 3. As can be seen from Fig. 3, the smaller the particle size, the faster the dissolution rate of Sb and As, and the higher the concentration of leaching solution.

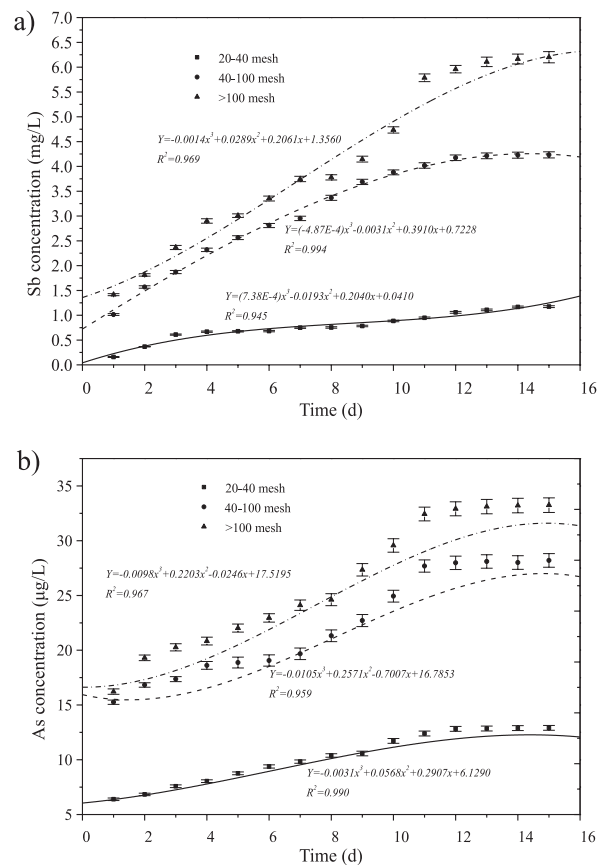


Fig. 3. Effect of particle size on a) Sb and b) As release in static experiment.

The regression fitting equation is shown in Fig. 3, in which the R^2 values of Sb and As regression release equation from waste rocks at different solid-liquid ratios were greater than 0.95 (except the fitting curve R2 of the change in Sb precipitation amount at the particle size of 20-40 mesh over time = 0.945), showing the better fitting effect.

The curve of Sb and As leaching concentration changing with time under different temperatures through soaking is shown in Fig. 4, where it can be seen that the higher the temperature, the easier the precipitation of heavy metal from antimony waste rocks. Because the dissolving process of antimony waste rocks in soaking

The regression fitting equation is shown in Fig. 4, in which the R^2 values of regression release equations of Sb and As under the influence of different temperatures is greater than 0.97, showing the better fitting effect.

The variation curve of Sb and As leaching concentration with time under static and perturbed soaking conditions is shown in Fig. 5. It could be seen in Fig. 5 that the amount of Sb and As precipitated from antimony waste rock under agitation conditions was greater than that under quiescence condition. Perhaps the main reason was that agitation improved the concentration gradient of liquid metal dissolved and precipitated from antimony waste rock, and raised the dissolving precipitation rate of heavy metals

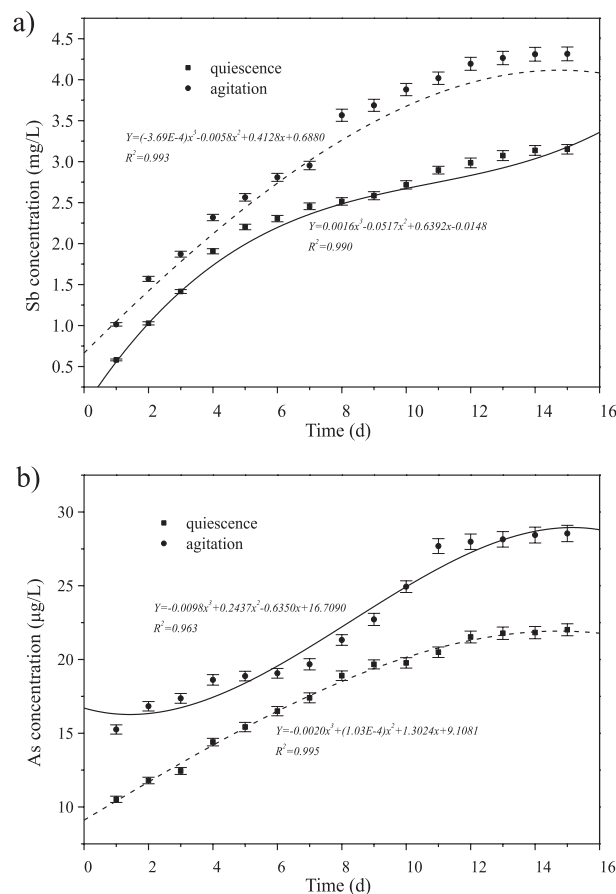


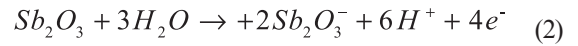
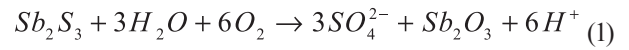
Fig. 5. Effect of agitation on a) Sb and b) As release in static experiment.

so as to improve the heavy metal concentration in soaking solution compared with that under quiescence conditions [21].

The regression fitting equation is shown in Fig. 5, in which the R^2 value of regression release equation of Sb and As under the influence of different temperatures was greater than 0.96, showing that the fitting effect was good.

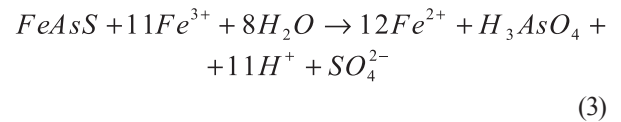
Effect of pH on Sb and As Release

The regularity of concentration changes of Sb and As in antimony waste rocks in different pH leaching solution is shown in Fig. 6. As could be seen from Fig. 6a), the change of Sb concentration in leaching solution was divided into two stages. In the initial stage of leaching (i.e., 1-3d), the Sb concentration in the three groups of experiments reached the maximum rapidly, namely, 31.058 mg·L⁻¹, 34.217 mg·L⁻¹ and 42.025 mg·L⁻¹ at pH = 4.0, pH = 5.0 and pH = 6.0, and this might be because the enamel microstructure on the surface of waste rock was damaged after 3 days of leaching, and the stibnite (Sb₂S₃) was oxidized to Sb₂O₃⁻¹ in oxygen-enriched environment, and then quickly entered into leaching solution, with the reaction formula as follows:



In the later stage of leaching (i.e., 4-12d), the leaching solution showed alkalescence due to the neutralization with alkaline carbonate minerals, so there was a certain amount of OH⁻ in the solution, and Fe³⁺ and Al³⁺ in leaching solution would react with OH⁻, generate Fe(OH)₃ and Al(OH)₃ colloid, and form a layer of thin film on the surface of smelting slag, so as to prevent further oxidation of stibnite; moreover, it could be seen that Sb concentration was inversely proportional to pH value, for which the reason was that Sb was a kind of amphoteric element, and Sb₂O₃⁻¹ generated in the leaching process of Sb in antimony waste rock was prone to form Sb(OH)₅ deposits, which could form soluble Sb(OH)₆⁻¹ at high pH. On the 12th day, the Sb concentrations in the three groups were respectively 19.687 mg·L⁻¹, 20.199 mg·L⁻¹, and 22.776 mg·L⁻¹ at pH = 4.0, pH = 5.0 and pH = 6.0.

It could be seen from Fig. 6 (b) that after 2d leaching of antimony waste rock, the As concentration in three groups of leaching solution at pH = 4.0, pH = 5.0 and pH = 6.0 reached the maximum, respectively, of 96.973 μg·L⁻¹, 104.608 μg·L⁻¹ and 107.097 μg·L⁻¹, and the main reason might be that the exchangeable As was oxidized and dissolved into leaching solution, with the specific reaction formula below:



The leaching concentration of As in waste rock began to decrease on the 3rd and 4th days, respectively. It might be that with the complete release of exchangeable As, other forms of As determined the concentration of As in leaching solution. In addition, with the progress of leaching, the oxidized AsO₄³⁻ was easily adsorbed by Al (OH)₃ and Fe(OH)₃ colloids, so the concentration of As ions in leaching solution became lower and lower.

Effect of Leaching Intensity on Sb and As Release

The change in the leaching precipitation of Sb and As from antimony waste rocks under different leaching intensities and times over time is shown in Fig. 7. It can be seen from Fig. 7 that the leaching precipitation process of Sb and As is different under different leaching intensities, and Sb and As concentrations precipitated from antimony waste rock under the action of low leaching intensity reached the peak at 3.16 h, which reached the peak at 7.07 h under the action of medium leaching intensity, and reached the peak at

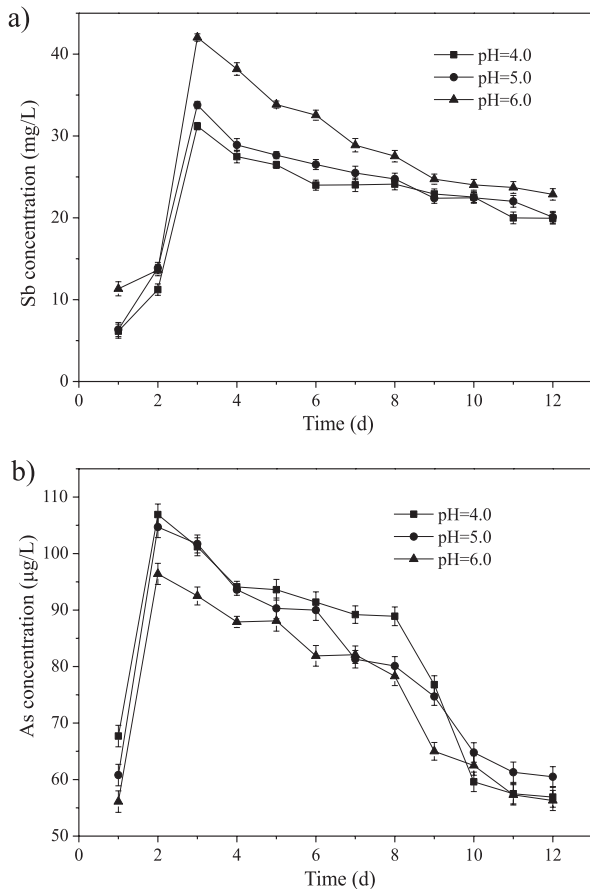


Fig. 6. Effect of pH on a) Sb and b) As release in dynamic experiment.

14.17 h under the action of high leaching intensity. Hereafter, the leaching precipitation of heavy metals gradually became stable under the action of different leaching intensities, for which the main reason might be that a dense enamel microstructure was formed on the surface of antimony waste rock in the process of mining, and the hydraulic shear force on the waste rock of high leaching intensity compared with that of middle and low leaching intensities, thereby having a stronger scouring force on the enamel microstructure of waste rock, so it is relatively easier for the heavy metals in antimony waste rock to reach the peak under the action of high leaching intensity.

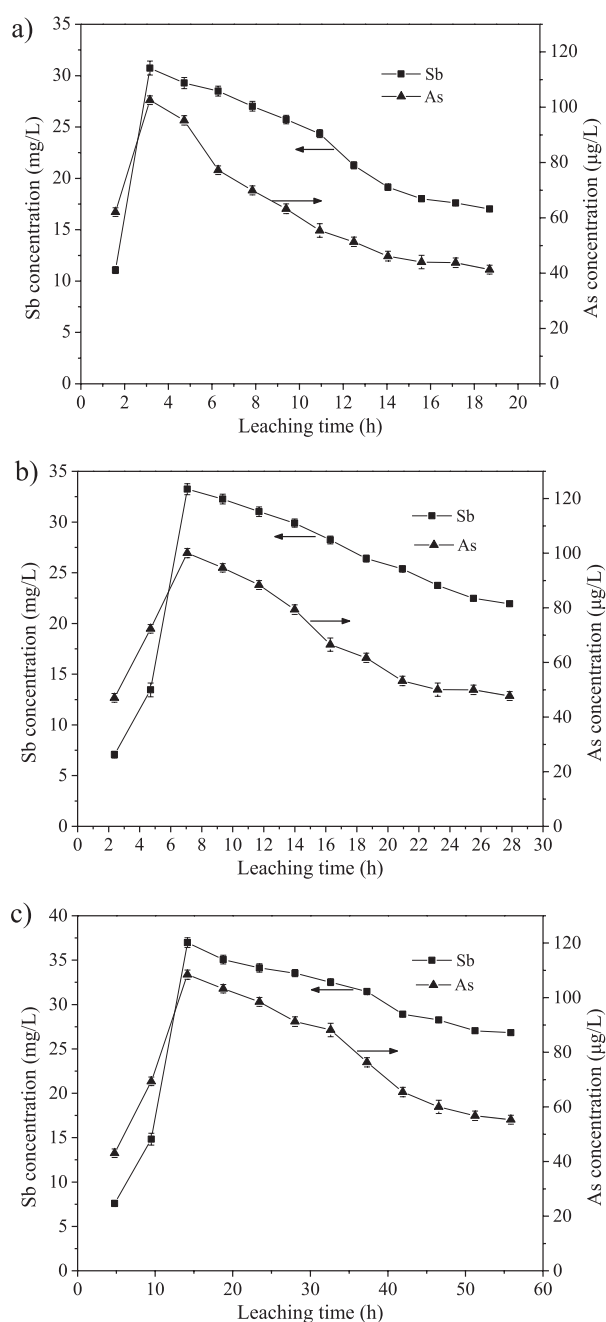


Fig. 7. Effect of leaching intensity on Sb and As release in dynamic experiment: a) 180 mL/h, b) 120 mL/h, c) 60 mL/h).

The cumulative release of Sb and As from antimony waste rocks in the leaching process was statistically measured (Table 1). It could be seen from Table 1 that, under the condition of stabilizing the leaching intensity at 180 mL/h, the cumulative release amount of As from 500 g antimony waste rock could reach 151.300 mg·kg⁻¹ at 18.70 hours of leaching time, and the cumulative precipitation amount of As could reach 428.880 µg·kg⁻¹; under the conditions of the leaching intensity being guaranteed to be 120 mL/h, the cumulative precipitation of Sb from 500 g antimony waste rock at 27.85 hours could reach 4.146 mg·kg⁻¹, and the cumulative precipitation of As could reach 451.804 µg·kg⁻¹. Under the conditions that the leaching intensity was guaranteed to be 60 mL/h, the cumulative release of Sb from 500 g antimony waste rock at 55.85 hours could reach 187.88 mg ·kg⁻¹, and the cumulative release of As could reach 510.902 µg·kg⁻¹ at most. As the passage of leaching time, the release amount of Sb and As showed an increasing tendency as a whole, and the mining waste rock was seriously eroded due to the increasingly enhanced leaching scouring action, so the water and air could enter inside the mining waste rock, and react with and its internal antimony compounds and arsenic compounds, and the long-lasting oxidation to Sb and As salts in waste rocks by water would cause more Sb and As being released from the waste rock due to oxidation reduction by water and air, and then enter the leaching solution, thus making the accumulative release amount increase. Under the rainy conditions in the south, the increase of rainfall will inevitably result in the relatively easier release of Sb and As from the waste rocks into the surrounding soil and water environment, thereby causing environmental pollution [22, 23].

Under different leaching conditions, the leaching release of Sb and As from antimony waste rocks (ensuring the same leaching intensity, 180 ml/h) can be conducted fitting with parabolic diffusion equation and Elovich equation $y(x)$, of which the independent variable x represents the time for reaching the soaking balance, and the dependent variable y represents the leaching concentration of each heavy metal. The regression fitting is shown in Fig. 8, in which the R^2 values of the regression release equations of Sb and As at different leaching times are over 93%, showing the better fitting effect (see Table 2).

Thus, the cumulative leaching amount of Sb and As in antimony waste rock in different leaching times is not a simple linear relationship. The leaching of heavy metal from antimony waste rock is a complicated process that involves vertical motion, horizontal diffusion and other physical processes; meanwhile, it also involves the adsorption/desorption, dissolution and precipitation, coordination complexation and other chemical processes, and the eventually cumulative leaching amount of heavy metals from antimony waste rock is a dynamic balance achieved by the interaction of physical and chemical factors [24, 25].

(3) The cubic polynomial fitting can be used to represent the change of Sb and As release amount from antimony waste rock under static soaking over time, and the R^2 values are greater than 0.950 (except the fitting curve R^2 of the change in Sb precipitation amount at the particle size of 20-40 mesh over time is 0.945), showing that the fitting effect is good. The release amount of Sb and As from antimony waste rocks under dynamic leaching can be conducted by fitting with parabolic diffusion equation and Elovich equation $y(x)$, and the R^2 values of regression release equations are greater than 93%, showing the better fitting effect.

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